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COMPOSITIONS FOR OPEN CROSSLINKING OF RUBBER AND CROSSLINKING METHOD

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Abstract

Objective

To provide compositions for open crosslinking of rubber and a crosslinking method capable of preventing the occurrence of tack on the surface of rubber products and, at the same time, maintaining excellent physical properties such as elasticity and tensile strength of the rubber products.

Means to solve [the problem]

The compositions for open crosslinking of rubber are formulated with compounds having phenylene groups and imino groups as the antioxidants for rubber, as well as with organic peroxides and crosslinking aids. As the antioxidants, benzimidazole compounds or polymers of 2,2,4-trimethyl-1,2-dihydroquinoline are preferred. As the crosslinking aids, maleimide compounds are preferred. The amount of incorporation for each component is preferably 0.5-2.0 parts by weight for the antioxidant, 1.0-4.0 parts by weight for the organic peroxide and 1.0-3.5 parts by weight for the crosslinking aid. And, by heating the composition in the atmosphere, a crosslinked rubber product can be obtained through crosslinking reaction.

Claims

- 1. Compositions for open crosslinking of rubber formulated with compounds having phenylene groups and imino groups as the antioxidants for rubber, as well as with organic peroxides and crosslinking aids.
- 2. Compositions for open crosslinking of rubber formulated with, based on 100 parts by weight of rubber, 0.5-2.0 parts by weight of one of the benzimidazole compounds having phenylene groups and imino groups and the chemical structures of (1)-(3) below, or a polymer of 2,2,4-trimethyl-1,2-dihydroquinoline having the chemical structure of (4) as the antioxidant, 1.0-4.0 parts by weight of an organic peroxide, and 1.0-3.5 parts by weight of a maleimide compound, as the crosslinking aid:

[Structure 1]

$$\bigcup_{N}^{H} c-sH \cdots (1)$$

[Structure 2]

[Structure 3]

$$\begin{bmatrix} H \\ \downarrow \\ N \\ C - S - \end{bmatrix}_{2} Z_{n} \qquad (3)$$

[Structure 4]

where n represents a number from 2-8.

3. An open crosslinking method of rubber by heating in the atmosphere the compositions for open crosslinking of rubber according to Claim 1 and Claim 2 to cause crosslinking.

Detailed explanation of the invention

[0001]

Technical field of the invention

This invention pertains to compositions for open crosslinking of rubber and a crosslinking method for the purpose of obtaining rubber products, by crosslinking rubber in the presence of hot air (hereafter, called open crosslinking). More particularly, it pertains to compositions for open crosslinking of rubber and a crosslinking method which makes it possible to eliminate surface tack on the rubber product by crosslinking with an organic peroxide.

[0002]

In general, when open crosslinking is carried out to form crosslinks for rubber, sulfur is added as the vulcanizing agent to yield crosslinked products having no tack on the surface. However, when an organic peroxide is used to replace sulfur, surface tack would occur on the rubber. The reason for this is that oxygen in the air inhibits the crosslinking reaction on the surface of the rubber, resulting in insufficient crosslinking necessary for a crosslinked product. Such finished products are not desirable as rubber products. Accordingly, crosslinking with

an organic peroxide for press molding and extrusion molding has been carried out in metal molding machines in the absence of oxygen.

[0003]

However, it is desirable to apply an open crosslinking method using an organic peroxide in order to improve physical properties such as the heat resistance of rubber products. In such case, in order to improve the surface tack property, a method of adjusting the amounts of the monomers of ethylene-propylene-diene copolymer rubber (hereafter called EPDM) (Japanese Kokai Patent Application No. Sho 64[1989]-75552 and Hei 4[1992]-293946) and one of adding silicone rubber and a bismaleimide compound (Japanese Kokai Patent Application No. Sho 58[1983]-13093) have been proposed.

[0004]

Additionally, methods adding multifunctional acrylic acid ester compounds and hindered amine compounds have also been proposed (Japanese Kokai Patent Application No. Hei 6[1994]-100741)

[0005]

Problem to be solved by the invention

However, in any of these methods, when crosslinking was carried out, crosslinks on the surface of the rubber were found

to be insufficient and there was a problem in that not only did surface tack occur, but at the same time, there were undesirable physical properties such as low tensile strength of the rubber products.

[0006]

Additionally, in the method of adjusting the amount of monomer, in the case of EPDM, if the amount of ethylene is too high, the rubber would become more plastic-like and there is concern that the characteristic elasticity of rubber will suffer. Also, in the methods of adding silicone rubber and bismaleimide compounds or adding hindered amine compounds, the addition of high-cost material like silicone rubber offers no advantage for manufacturing rubber having a wide range of applications.

[0007]

This invention was one carried out by focusing on such problems existing in the conventional techniques. The set objective was to provide compositions for open crosslinking of rubber and a crosslinking method capable of preventing the occurrence of tack on the surface of rubber products, and at the same time, maintaining excellent physical properties such as elasticity and tensile strength of the rubber products. Still another set objective was to provide compositions for open crosslinking of rubber and a crosslinking method capable of performing open crosslinking at a sufficiently high crosslinking rate for inexpensive rubber for a wide range of applications.

[8000]

Means to solve the problems

In order to achieve the aforementioned objective, the compositions for open crosslinking of rubber of Claim 1 were formulated with compounds having phenylene group and imino group as the antioxidants for rubber, as well as with organic peroxides and crosslinking aids.

[0009]

The compositions for open crosslinking of rubber of Claim 2 were formulated with, based on 100 parts by weight of rubber, 0.5-2.0 parts by weight of a benzimidazole-type compound having phenylene groups and imino groups and the chemical structure of (1)-(3) below, or a polymer of 2,2,4-trimethyl-1,2-dihydroquinoline having the chemical structure of (4), as the antioxidant, 1.0-4.0 parts by weight of an organic peroxide, and 1.0-3.5 parts by weight of a maleimide compound, as the crosslinking aid.

[0010]

[Structure 5]

$$\bigcup_{N}^{H} C-SH \cdots (1)$$

[0011]

[Structure 6]

$$H : C \longrightarrow N - SH - \cdots (2)$$

[0012]

[Structure 7]

$$\begin{bmatrix} H \\ | \\ N \\ C - S - \end{bmatrix}_{2} Z_{n} \qquad \cdots \qquad (3)$$

[0013]

[Structure 8]

Where n represents a number of 2-8. The open crosslinking method of Claim 3 is one of carrying out crosslinking reaction by heating the compositions of Claims 1 and 2 for open crosslinking of rubber in the presence of air.

[0014]

Embodiments of the invention

The conditions of application of the present invention are explained in detail in the following. The compositions for open crosslinking of rubber were formulated with compounds having phenylene groups and imino groups as the antioxidants for rubber, as well as with organic peroxides and crosslinking aids.

[0015]

First of all, although any rubber that can be crosslinked with organic peroxides may be used, those having a diene component are more appropriate because they can be crosslinked with good efficiency. As specific examples of such rubber containing dienes, EPDM, acrylonitrile-butadiene copolymer rubber (hereafter abbreviated as NBR), ethylene-propylene rubber, natural rubber, butadiene rubber, and styrene-butadiene may be cited.

[0016]

Secondly, antioxidants are the ones that primarily prevent oxidation from occurring on the surface of the rubber and

maintain the crosslinking reaction, while inhibiting the occurrence of tack on the surface of the rubber products. The antioxidants are compounds having phenylene groups or imino groups. Specifically, they are the benzimidazole compounds having the aforementioned structures (1)-(3), and polymers of 2,2,4-trimethyl-1,2-dihydroquinone having structure (4). In structure (4), if n is higher than 8, then its dispersion in rubber becomes undesirable.

[0017]

At least one of these compounds is formulated into the aforementioned rubber. The benzimidazole compounds are 2-mercaptobenzimidazole of structure (1), 2-mercaptomethylbenzimidazole of structure (2) and the zinc salt of 2-mercaptobenzimidazole of structure (3). Among these chemicals, polymers of 2,2,4-trimethyl-1,2-dihydroquinoline are preferred because of their high effectiveness as antioxidants. Additionally, as the benzimidazole compounds, 2-mercaptoethylbenzimidazole or the iron salt of 2-mercaptobenzimidazole may be used.

[0018]

The amount of addition of the antioxidant is 0.5-2.0 parts by weight, and preferably 1.0-2.0 parts by weight, based on 100 parts by weight of the rubber composition. At a concentration under 0.5 part by weight, the rubber product would exhibit tack on the surface, and above 2.0 parts by weight, the crosslinking reaction is hindered.

[0019]

The organic peroxides are the ones to induce the crosslinking reaction. As examples,

1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane,

n-butyl-4,4-bis(t-butylperoxy)valerate,

α,α-bis(t-butylperoxy)diisopropylbenzene, dicumylperoxide,

2,5-dimethyl-2,5-di(t-butylperoxy)hexane, t-butylcumylperoxide,

di-t-butylperoxide, and

2,5-dimethyl-2,5-di(t-butylperoxy)hexene-3, and

1,6-bis(t-butylperoxycarbonyloxy)hexane may be cited.

[0020]

Among said organic peroxides, the dialkylperoxides such as α,α' -bis(t-butylperoxy)diisopropylbenzene, dicumylperoxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, t-butylcumylperoxide, di-t-butylperoxide, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexene-3 are preferred. This is because these dialkylperoxides decompose at relatively high temperatures, and the free radicals so obtained have a strong ability to extract hydrogen atoms.

[0021]

The amount of addition of the organic peroxides is 1.0-4.0 parts by weight, and preferably 1.0-3.5 parts by weight, based on 100 parts by weight of rubber. At concentrations under 1.0 part by weight, there would be insufficient crosslinking,

while at more than 4.0 parts by weight, it would result in a problem of substantial decrease of the tensile property.

[0022]

Furthermore, the crosslinking aids are ones used to increase the rate of crosslinking of the crosslinking reaction. As examples, methacrylate esters such as trimethylolpropane trimethacrylate and ethyleneglycol dimethacrylate, and vinyl monomers such as triallylcyanurate and triallylisocyanurate, and maleimides such as N,N-m-phenylene-bismaleimide may be cited. Among these crosslinking aids, maleimides such as N,N-m-phenylene-bismaleimide are preferred for their abilities not only to increase the rate of crosslinking, but also to improve the physical properties such as the tensile strength of the rubber products.

[0023]

The amount of addition of the crosslinking aids is 1.0-3.5 parts by weight, and preferably 1.0-3.0 parts by weight, based on 100 parts by weight of rubber. At an amount of addition under 1.0 part by weight, there would be insufficient crosslinking reaction and the surface [of the rubber] would exhibit tack. At above 3.5 parts by weight, the crosslinking reaction would progress excessively, injuring the properties of the rubber.

[0024]

If necessary, carbon black (hereafter abbreviated CB), or silica (obtained by a dry method or wet method) as a whitening filler, silicates such as clay, or carbonates such as calcium carbonate and magnesium carbonate may be incorporated in the compositions for open crosslinking of rubber.

[0025]

Furthermore, if necessary, softening agents such as liquid paraffin or polymeric softening agents such as paraffin-type process oil may be incorporated. Mixing of the antioxidant, organic peroxide, and crosslinking aid to be added to the rubber was carried out by using a roller, a Banbury mixer or a kneader.

[0026]

As the apparatus for open crosslinking, a hot air oven or hot-air-type heating oven equipped with a preheating device such as a microwave heater (high frequency) (for example, the MMV model from Mikuro Denshi Co., which is a device that preheats with microwaves, followed by crosslinking using hot air), a far-infrared heater or an electric heater.

[0027]

It is desirable that the crosslinking temperature is from 180°C to 220°C and that the time of crosslinking is from 5 min to 10 min. Said crosslinking temperature was established from the

viewpoint that it is necessary to complete the crosslinking reaction in a short period of time at high temperature because the open crosslinking is being conducted in the presence of hot air. However, it is not desirable if the temperature is over 220°C, because in addition to the crosslinking of the rubber, oxidation of the rubber itself would also be promoted. On the other hand, it is undesirable if it is below 180°C because the rate of the crosslinking reaction becomes too slow.

[0028]

According to the above application conditions, the following effects are achieved.

- (1) The compositions for open crosslinking of rubber can perform sufficient crosslinking reaction by protecting the surface from being oxidized with an antioxidant and by accelerating the rate of crosslinking with a crosslinking aid, and the occurrence of tack on the surface of the rubber can be prevented.
- (2) By using an organic peroxide or antioxidant in the crosslinking, excellent physical properties of the rubber products such as rubber elasticity, tensile strength and heat resistance can be fully realized.
- (3) Open crosslinking can be easily carried out at a sufficiently high rate of crosslinking for manufacturing inexpensive rubber having broad applications.
- (4) Therefore, productivity can be improved for open crosslinking of rubber, by using an organic peroxide.

[0029]

Application examples

The present invention is further illustrated below in more detail using application examples and comparative examples.

Unless it is otherwise specified, these portions in the application examples and comparative examples are all expressed in parts by weight. Also, in the application examples and comparative examples, the following methods were used for preparation of the samples, or as crosslinking methods, or as the methods for the evaluations of the physical properties.

Preparation of samples

A 6-in roller was used to knead 100 parts by weight of rubber alone. Given amounts of an antioxidant, an organic peroxide and a crosslinking aid were then added and the mixture was kneaded to produce noncrosslinked rubber in sheet form of 2 mm in diameter.

Open crosslinking

The rubber sample in sheet form was placed in a 200°C gear-type aging tester (Toyo Seiki Co. product, GO-01 model), and open crosslinking reaction was carried out for 5 min at a temperature 20°C above the one minute half-life temperature to yield crosslinked rubber sheet.

Surface properties

The change of viscosity of the rubber during the course of crosslinking reaction was determined with a pendulum using a rigid-body pendulum-type elasticity testing device (Toyo Yushi Co. Ltd. Product, Reoba Ibu Naron-OPA [transliteration]) and the surface properties were evaluated. The results were evaluated based on the following standards.

[0030]

0: No tack at all, o: very slight tack, $\Delta:$ some tack, x: very high tack.

Tensile test

The obtained crosslinked product was made into JIS No. 3 dumbbell test pieces, and the tensile property was determined by the JIS K 6251 [method].

[0031]

The raw materials used were as follows:

| NAME | TRADE NAME | MANUFACTURER NAME |
|---------------|---------------------------------------|----------------------------|
| EPDM | : EPT-4021 | Mitsui Sekiyu Kagaku Kogyo |
| •. | | K.K. |
| NBR | : DN207 | Nippon Zeon K.K. |
| Silica | : Zeosil 500V | Tagi Kagaku K.K. |
| Carbon black | : Asahi #70 | Asahi Carbon K.K. |
| Antioxidant-1 | : Nocrack 224 | Ouchi Shingyo Kagaku K.K. |
| | (2,2,4-trimethyl-1,2-dih | nydroquinoline polymer) |
| Antioxidant-2 | : Nocrack MB | Ouchi Shinko Kagaku K.K. |
| | (2-mercaptobenzimidazole | a) |
| Crosslinking | į. | |
| aid-1 | : N,N-m-phenylene | |
| | -bismaleimide | Wako Junyaku K.K. |
| Crosslinking | | |
| aid-2 | : Triallylcyanurate | Wako Junyaku K.K. |
| Organic | | |
| peroxide-1 | : Per-Butyl P | Nippon Yushi K.K. |
| _ | $(\alpha, \alpha'$ -bis(t-butylperoxy | diisopropylbenzene) |
| | 1 min half-life tempera | |

Organic

peroxide-2 : Per-Cumyl D Nipp

Nippon Yushi (Oils and

Fats) K.K.

(dicumylperoxide)

1 min half-life temperature (175°C)

Organic

peroxide-3 : Per-Hexa 25B

Nippon Yushi (Oils and

Fats) K.K.

(2,5-dimethyl-2,5-(t-butylperoxy)hexane)

1 min half-life temperature (180°C)

Application Examples 1-6 and Comparison Examples 1-6

A compounded rubber sheet of 2 mm in thickness was prepared by kneading EPDM, antioxidant, organic peroxide, crosslinking aid, and silica or carbon black using a 6-in double roller. Crosslinked product was obtained by open crosslinking for 5 min at 200°C in a gear-type aging tester. The surface condition was evaluated using a rigid-body pendulum, and the tensile property of the crosslinked product was determined by JIS 6251. The results are shown in Tables I-III. In the following tables, T_B denotes the tensile strength of the rubber, and E_B denotes the elongation at break of the rubber.

[0032]

Table I

| 1 | · · | ① 実 施 例 | | | | | | | | | |
|-----------------|--|-------------------------|-------------------------|--|---------------------------|--|------------------------------|-------------------------|---|--|--|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | | |
| 30 D WOOD | BPDM 対力 シーメンプラッと 砂化防止剤-1 酸化防止剤-2 契抵助剤 -2 有機過過酸化物-2 有機過酸化物-2 有機過酸化物-3 | 100 40 0.5 3.5 | 100 40 1.0 3.0 | 100 40 2. 0 - 2. 0 1. 7 | 100 40 2. 0 1. 0 | 100 40 - 1.0 - 2.0 1.7 | 100 40 - 1.0 2.0 | 100 40 1.0 2.0 | 1.0 - 1.0 - 2.0 - 2.5 | | |
| \widecheck{o} | 引張試驗 TB(kg/cm²) EB(%) | 63. 1 210 | 61. 4 200 | 58. 1 250 | 55. 6 260 | 57. 9 240 | 61.3 270 | 45. 2 290 | 77. 1 220 | | |
| (12) | 表面性評価 | 0 | 0 | 0 | © | 0 | 0 | 0 | <u>©</u> | | |

- Application example Key: 1
 - Silica 2
 - Carbon black 3
 - Antioxidant-1
 - Antioxidant-2 5
 - Crosslinking aid-1 6
 - Crosslinking aid-2 7
 - Organic peroxide-1 8
 - Organic peroxide-2 9
 - Organic peroxide-3 10
 - Tensile experiment
 - 11
 - Evaluation of surface property 12

[0033]

Table II

| | | ① 実 施 例 | | | | | | | | | |
|---|--------------------------------|--|---|------------------------------|-----------------------------------|--------------------------------------|---|--|--|--|--|
| | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | | | |
| EPDM シッカーシブラック かーキンブラック が かーキンブラック が かートンファック が かートンファック の かートンファック の かートンファック の かートンファック の かった アンファック の かった アンファック | 100 40 1.0 2.0 3.5 | 100 40 1.0 - 2.0 - 4.0 | 100 40 - 1.0 - 2.0 - 2.5 | 100 40 1.0 - 2.0 | 100 -40 1.0 -2.0 -1.7 | 100 -40 1.0 - 2.0 1.7 | 100 -40 1.0 - 2.0 - 2.5 | 100 40 1.0 - 2.0 - 3.0 | | | |
| 引張試験 TB(kg/cm²) EB(%) | 80. 5 190 | 81. 0 130 | 63. 9 200 | 57. 1 230 | 45. 6 190 | 43.9 170 | 44.3 190 | 40.1 190 | | | |
| 表面性評価 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | | |

- Application example Key: 1
 - Silica 2
 - Carbon black 3
 - Antioxidant-1 4
 - Antioxidant-2 5
 - Crosslinking aid-1 6
 - Crosslinking aid-2 7 .
 - Organic peroxide-1 8
 - Organic peroxide-2 9
 - Organic peroxide-3 10
 - Tensile experiment 11

 - Evaluation of surface property 12

[0034]

Table III

| [| | | ① H | 比較 | 9 9] | | |
|-----------|---|-------------------|-----------------------|---------------|-----------------------------------|-------------------|--------------|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| මලමට ලෙලල | 8PDM かまが5ック 酸化防力・1 酸化防力・2 架橋機過酸化物-1 有機過過酸化物-2 有機過過酸化物-3 | 1.00 40 1.0 | 100 40 - 1.0 | 100 40 | 100 40 - - 2.0 1.7 | 100 40 1. 0 | 1.0 |
| <u> </u> | 引張試験 TB(kg/cm²) EB(%) | 37. 2 350 | 40. 2 480 | 68. 9 240 | 65. 2 240 | 34. 1 360 | 32. 6 380 |
| 12) | 表面性評価 | × | × | · × | × | × | × |

| Key: 1 | Comparison | example |
|--------|------------|---------|
| 2 . | Silica | - |
| | | • |

- 3 Carbon black
- 4 Antioxidant-1
- 5 Antioxidant-2
- 6 Crosslinking aid-1
- 7 Crosslinking aid-2
- 8 Organic peroxide-1
- 9 Organic peroxide-2
- 10 Organic peroxide-3
- 11 Tensile experiment
- 12 Evaluation of surface property

Application Examples 17-25

Crosslinking products were obtained in the same manner as that in Application Examples 1-16 except that NBR was used to replaced EPDM, and the surface condition and tensile property were determined. The results are shown in Table IV.

[0035]

Table IV

| | · | | | | | | : | | | |
|---------------|---|-------------------------|-------------------------|------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|------------------|------------------|
| ſ | | | | <u> </u> |)実 数 | #1 | | <u> </u> | | 25 |
| t | | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | |
| මෙමෙන්ම ලෙලු | RBR ラリカカーよびラック 放化防止剤 -1 (25) 機能助剤 -2 (25) 神経 -1 (25) | 100 40 1.0 2.0 | 100 40 2.0 1.0 | 100 40 - 1.0 2.0 | 100 40 1.0 2.0 | 100 40 1.0 2.0 | 100 40 1.0 2.0 | 100 40 1.0 2.0 | 40 1.0 2.0 | 40 1.0 2.0 |
| 3000 E | 架橋助剤 -2 有機過酸化物-1 有機過酸化物-2 有機過酸化物-3 | 1.7 | 1.7 | 1.7 | 2. 5 - - - | 2. 5 | 3.0 | 1.7 | 2.5 | 3. 0 |
| (E) | 引張試験 TB(kg/cm²) EB(%) | 53. 9 230 | 50. 6 240 | 59. 8 270 | 60.3 220 | 59. 9 210 | 56. 3 230 | 41. 9 220 | 45. 6 220 | 43.9 230 |
| <u>(2</u> | 表面性評価 | 0 | 0 | 0 | 0 | 0 | <u>©</u> | 0 | <u> </u> | <u> </u> |

Application example Key: 1 Silica Carbon black 3 Antioxidant-1 Antioxidant-2 Crosslinking aid-1 Crosslinking aid-2 7 Organic peroxide-1 Organic peroxide-2 Organic peroxide-3 10 Tensile experiment 11

Evaluation of surface property

Application Examples 26-43

12

Crosslinking products were obtained in the same manner as that in Application Examples 1-16 except that the formula amounts of antioxidant, crosslinking aid and organic peroxide were varied, and the surface condition and tensile property were determined. The results are shown in Tables V-VII.

[0036]

Table V

| ſ | | | 0 | 実 | 施例 | | |
|-----------|---|-------------------------|---------------------------|-------------------------|-------------------------|--------------------------------|--|
| ļ | | 26 | 27 | 28 | 29 | 30 | 31 |
| මළුවල ලෙළ | BPDM かまが75・79 酸化化防助剂 -1 気候核助助過酸酸化物 -2 有核機過過酸酸化物-2 有機機過酸酸化物-2 有機機過 | 100 40 0.3 2.0 | 100 40 2. 5 2. 0 | 100 40 1.0 0.5 | 100 40 1.0 4.0 | 100 40 1.0 2.0 0.5 | 100 40 - 1.0 2.0 - 4.5 |
| ① | 引張試験 TB(kg/cm²) EB(X) | 67. 1 230 | 49. 7 260 | 37. 5 370 | 71.1 180 | 21. 3 350 | 81.9 110 |
| (| 表面性評価 | Δ | Δ | Δ | Δ | Δ | 0 |

Application example Key: 1 Silica 2 Carbon black 3 Antioxidant-1 4 Antioxidant-2 5 Crosslinking aid-1 Crosslinking aid-2 Organic peroxide-1 8 Organic peroxide-2 9 Organic peroxide-3 10 Tensile experiment 11 Evaluation of surface property

12

[0037]

Table VI

| | ①奥 | 施罗 | |
|--|--|--|--|
| | 32 | 33 | 34 |
| BPDM リカ カーギンブラック 酸 化化防防 期子 1 会 に を で で で で で で で で で で で で で で で で で で | 100 40 1.0 0.5 1.7 | 100 40 1.0 0.5 | 100 - 40 1.0 - 0.5 - - 3.0 |
| 引張試験 TB(kg/cm²) EB(%) | 40. l 240 | 38. 9 240 | 38. 0 250 |
| 表面性評価 | Δ | Δ | Δ |
| | リカ カーシンプラック カーシンプラック 対した 、 、 、 、 、 、 、 、 、 、 、 、 、 、 、 、 、 、 、 | 32 BPDM 100 10 | 32 33 33 35 35 35 35 35 |

Application example Key: 1 Silica 2 Carbon black 3 Antioxidant-1 4 Antioxidant-2 5 Crosslinking aid-1 6 Crosslinking aid-2 7 Organic peroxide-1 8 Organic peroxide-2 9 Organic peroxide-3 10 Tensile experiment 11 Evaluation of surface property

12

[0038]

Table VII

| ſ | | | | 0 | 実 施 | 例 | | | | |
|---|---|--|--------------------------------|-------------------------|-------------------------|---|---|--------------------------------|--|-------------------------------|
| ł | | . 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 |
| =)(e)(e)(a)(a)(a)(a)(a)(a)(a)(a)(a)(a)(a)(a)(a) | HBR カーボブラック かーボブラック かーボブラック 一・ボーク ・・・・・・・・・・・・・・・・・・・・・・・・・・・・・・・・・・・・ | 100 40 - 0. 3 - 2. 0 - 1. 7 | 100 40 2.5 2.0 1.7 | 100 40 1.0 0.5 | 100 40 1.0 4.0 | 100 40 - 1.0 - 2.0 - 0.5 | 100 40 - 1.0 - 2.0 - 4.5 | 100 40 1.0 0.5 1.7 | 100 40 1.0 - 0.5 - 2.5 | 100 1.0 0.5 - 3.0 |
| (=) | 引張試験 TB(kg/cm²) EB(X) | 57. 1 230 | 51.3 240 | 33. 9 270 | 60. 3 210 | 23. 1 320 | 75.3 140 | 36. 6 240 | 34. 1 240 | 33.0 260 |
| 2 | 表面性評価 | Δ | Δ | Δ | Δ | Δ | 0 | Δ | Δ | |

Key 1 Application example
2 Silica
3 Carbon black
4 Antioxidant-1
5 Antioxidant-2
6 Crosslinking aid-1
7 Crosslinking aid-2
8 Organic peroxide-1
9 Organic peroxide-2
10 Organic peroxide-3

Tensile experiment

Evaluation of surface property

11

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As shown in Application Examples 1-25 in Tables I, II, and IV, all the rubber products exhibited excellent tensile strength, elongation at break, and surface property. Thus, the occurrence

of tack on the surface of the crosslinking product was inhibited, and the crosslinked rubber products showed excellent physical properties. Furthermore, as shown in Application Examples 26-43 in Tables V-VII, even if one of the formula amounts of antioxidant, crosslinking aid or organic peroxide was not in the desirable range, the surface property and the physical property of the crosslinked rubber could still be maintained in the designated ranges.

[0039]

On the other hand, in Comparative Examples 1-6 in Table III, since no antioxidant, crosslinking aid, or organic peroxide is mixed, the surface property of the rubber products is poor and the physical properties of the rubber products are lowered.

[0040]

Accordingly, the technical knowledge acquired from the aforementioned application conditions are listed in the following.

- (1) A composition for open crosslinking of rubber according to Claim 2 where the maleimide compound is N,N-m-phenylene-bismaleimide. Using this composition, the rate of crosslinking can be increased, and at the same time, the physical properties of the rubber such as the tensile strength can also be improved.
- (2) A manufacturing method of rubber products in which the open crosslinking compositions for rubber according to Claim 1 and Claim 2 are heated in the presence of air to induce

crosslinking reaction. Using this manufacturing method, the tack on the surface can be prevented, and at the same time, rubber products having excellent physical properties such as tensile strength can be easily obtained.

[0041]

Effect of the invention

As has been described in detail in the above, according to the present invention, the following excellent effects can be achieved. Using the compositions for open crosslinking of rubber according to Claim 1, the occurrence of tack on the surface of the rubber products can be prevented, and at the same time, the rubber products can exhibit fully their excellent physical properties such as rubber elasticity and tensile strength.

[0042]

According to Claim 2, the effects of Claim 1 can be further increased. According to the crosslinking method of Claim 3 for the compositions for open crosslinking of rubber, inexpensive rubber having a wide range of applications can be easily open crosslinked at a sufficiently high rate of crosslinking.